Effect of electron irradiation on the transformation characteristics of narrow hysteresis TiNiCu shape memory alloys

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TiNiCu shape memory alloy samples were irradiated by 1.7 MeV electrons below the martensite finish temperature M_f. The transformation temperatures and the latent heat of phase transformation were measured by differential scanning calorimeter. The damage accumulation was determined by positron annihilation technology. The results indicated that the austenite transformation temperatures were raised, and the hysteresis was increased by the irradiation. The electron irradiation had a slight effect on M_f, and no detectable effect on the martensitic transformation start temperature M_s. The second lifetime of positrons were increased by the electron irradiation indicating the increase in the size and amount of vacancy clusters, which contributed to the observed change of the transformation characteristics. © *2002 American Institute of Physics.*
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Coupling devices and actuators using shape memory alloys (SMAs) are attracting interest for applications in the fields of nuclear engineering and space technology.[1–3] For this purpose, it is necessary to know the effect of irradiation on the shape memory behavior of the alloys. There have been several studies on the change of shape memory characteristics of TiNi and CuZnAl SMAs after neutron, proton and electron irradiation.[2–10] The results indicated that the irradiation can have a very strong influence on the transformation temperatures and the mechanical behavior of SMAs.

Comparing with TiNi and Cu-base SMAs, the ternary TiNiCu shape memory alloy has a much smaller hysteresis in transformation temperatures and pseudoelasticity and a much lower flow stress for martensitic reorientation. It is also much less sensitive to aging effects.[3] Therefore, TiNiCu is a better candidate for many applications such as electrical connectors, sensors and actuators. Unlike the near equal atomic TiNi alloys, the martensitic transformation in this TiNiCu alloy is from B2 to B19, without Ti_3Ni_4 precipitation and *R*-phase transformation.[3,4] Thus, its irradiation effect might be different from that in TiNi. However, as far as the authors' knowledge is concerned, the irradiation effect of TiNiCu SMA has not been reported. In this work, the irradiation effect on the transformation temperatures, the latent heat of phase transformation and the defect production of TiNiCu SMA have been studied by means of 1.7 MeV electron electrostatic accelerator, differential scanning calorimeter (DSC) and positron annihilation technology (PAT).

Ti–43 at. % Ni–7 at. % Cu SMA samples with a thickness of 0.30 mm, provided by the Northwest Institute of Non-Ferrous Metal of China, were annealed at 773 K for 30 min in an evacuated silica tube and then cooled in the air. As shown in Table I, after the heat treatment, the samples were then irradiated in air to the electron dose ($E=1.7$ MeV) of 5.5, 11.1, and 17.4 ($\times 10^{20}$ m^{-2}) at the dose rate of 4.4×10^{16} $m^{-2}s^{-1}$ in the Electron Electrostatic Accelerator of the Key Laboratory for Radiation Physics and Technology of Education Ministry of China located in Chengdu. The temperature of the samples during the irradiation was controlled by circulating water and was maintained at about 298 K monitored by a thermocouple, well below the martensitic transformation finish temperature M_f (shown in Table II). Thus, the samples have been kept in the martensitic phase during the electron irradiation.

The irradiated samples were placed at room temperature for about 20 days then, the transformation temperatures were measured by DSC between 200 and 400 K at a rate of 10 $K\,min^{-1}$.

On a conventional fast–fast coincidence setup (ORTEC) with NEIII scintillators and a time resolution of 235 ps, the positron annihilation lifetime was measured at room tem-

TABLE I. Experimental conditions of the electron irradiation.

Samples	Conditions of the electron irradiation with an energy of 1.7 MeV and a dose rate of 4.4×10^{16} $m^{-2}s^{-1}$
1	Unirradiated
2	Irradiated for 3.5 h to a dose of 5.5×10^{20} m^{-2}
3	Irradiated for 7 h to a dose of 11.1×10^{20} m^{-2}
4	Irradiated for 11 h to a dose of 17.4×10^{20} m^{-2}

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TABLE II. Transition temperatures of the martensitic transformations of TiNiCu SMA samples, before and after electron irradiation, measured by DSC.

Samples	Dose (10^{20} m^{-2})	A_s (K)	A_f (K)	M_s (K)	M_f (K)
1	0	322	336	318	305
2	5.5	325	339	318	304
3	11.1	334	346	320	311
4	17.4	335	346	319	309

perature with the source ^{22}Na sandwiched between two electropolished, identical samples. The computer program, Positronfit, was used for the lifetime spectrum fitting with a total count over 10^6.

The DSC curves of the electron irradiated and the unirradiated samples are shown in Fig. 1. The transformation temperatures are listed in Table II (M_s, M_f and A_s, A_f is the martensitic transformation start, finish temperature and austenite transformation start, finish temperature, respectively). The positron annihilation second lifetime of the samples is shown in Fig. 2.

It is obvious from Fig. 1 and Table II that the transformation temperatures A_s, A_f, and M_f of TiNiCu SMA were increased by the electron irradiation but the irradiation up to the dose of 17.4×10^{20} m^{-2} had no detectable effect on M_s so the martensitic phase was stabilized[11–13] by the irradiation in the sense that the reverse transformation temperatures were higher than before. This is different from the results of neutron irradiated TiNi SMA, for which a strong decrease of the transition temperatures was observed.[6]

Figure 2 shows clearly that the defect lifetime τ_2 increased with the irradiation dose. This implies that the size and the amount of the vacancy clusters in the samples had been increased by the irradiation.[14] Moreover, the unirradiated sample had a τ_2 of about 300 ps, so the vacancies in the

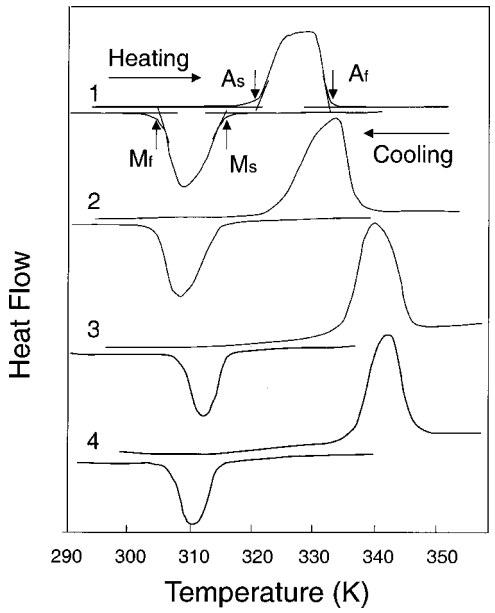

FIG. 1. DSC results of TiNiCu specimen showing that the martensitic transformation was shifted to higher temperatures after electron irradiation: (1) unirradiated, (2), (3), (4) are from samples irradiated to 5.5, 11.1, 17.4 $\times10^{20}$ m^{-2}, respectively. The characteristic temperatures (M_s,M_f,A_s,A_f) of the transformation are listed in Table I.

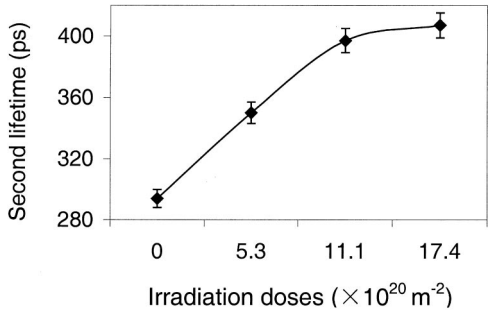

FIG. 2. Increase of the positron annihilation second lifetime (ps) of TiNiCu SMA samples with the electron irradiation doses.

sample are so-called divacancy or vacancy clusters.[15] This might be mainly due the internal twin or slip structures of its orthorhombic B19 martensite and the twin boundaries between martensitic variants. Since the range of the 1.7 MeV electron beam (~1 mm)[16] is much larger than the thickness of the samples (~0.3 mm), the electrons had penetrated through the whole sample and had produced evenly distributed Frenkel point defects (interstitials and vacancies). Some point defects may migrate to the exiting microstructure defects (twin boundaries and dislocations) modifying the local atomic configuration, and some may accumulate to form defect clusters.

Since the amount of the changes in the transformation temperatures $M_{s,f}$ and $A_{s,f}$ are not all the same, the electron irradiation had affected the transformation hysteresis defined by A_s-M_s or A_f-M_s and the stored elastic energy related to M_s-M_f or A_f-A_s. The equilibrium temperature T_0 between the martensitic and the parent phase is the temperature at which the Gibbs free energies (the chemical term) of the two phases are equal,[3,17] which is approximately equal to $1/2(M_s+A_f)$.[17,18] The hysteresis in the transformation can be represented by the overheating $A_f-T_0=1/2(A_f-M_s)$ which is related to the driving force for the nucleation of the parent phase.[18]

Table III lists the values of T_0, A_f-T_0, M_s-M_f, and A_s-M_s of the samples calculated from Table II, it is clear that the thermodynamic equilibrium temperature T_0 of the martensitic and the parent phase was raised by the electron irradiation. Thus, the martensite was stabilized by the electron irradiation[12,19] and the Gibbs free energy of the martensite was lowered with respect to the parent phase, which led to a higher equilibrium temperature T_0. This might be due to the irradiation induced disordering of the crystallographic structure.

Table III shows that the hysteresis of the martensitic phase transformation A_f-T_0 and A_s-M_s had been increased significantly by the electron irradiation. At the same time

TABLE III. Irradiation effects on T_0, A_f-T_0, A_s-M_s, and M_s-M_f of TiNiCu SMA samples calculated from Table II.

Samples	Dose (10^{20} m^{-2})	T_0 (K)	A_f-T_0 (K)	A_s-M_s (K)	M_s-M_f (K)
1	0	327	9	3	14
2	5.5	328	11	7	14
3	11.1	333	13	13	9
4	17.4	333	13	16	10

$M_s - M_f$ had decreased slightly after 7 h electron irradiation for dose values of 11.1 and 17.40 ($\times 10^{20}$ m^{-2}). As indicated by the positron annihilation measurement of Fig. 2, the irradiation raised the size and amount of vacancy clusters to resist the phase transformation. This would result in a higher driving force needed for the austenite nucleation, thus a larger overheating $A_f - T_0$. On the other hand, since the irradiation was performed in the martensitic phase of the sample, some of the point defects produced by the electron irradiation would migrate to the exiting twin boundaries of martensite leading to a relaxation of the stored elastic energy and a slight decrease of $M_s - M_f$.[7]

The electron irradiation increased the austenite transformation temperatures and hysteresis of TiNiCu SMAs, and had a slight effect on M_f and no effect on M_s. Thus, the martensite was stabilized by the irradiation. The overheating needed for the austenite nucleation was raised by about 50% and the difference between M_s and M_f decreased by 30% after the irradiation by electrons to a dose of 11.1 $\times 10^{20}$ m^{-2}.

The results of positron annihilation spectroscopy had shown that the second lifetime of positrons was increased by the electron irradiation so, the size and amount of vacancy clusters was raised and this contributed to the observed change of the transformation characteristics of the electron irradiated TiNiCu SMAs.

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